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(G) Cest stainless steel alloy and method for its manufacture.

(5) Cest metal parts such as turbocharger housings which ers subject to operating temperatures up to about 2000°F (1093°C) and require good thermal cyclic durability (resistance to thermal cracking) and burst containment properties, are made from a low nickel duplex stainless steel with nitrogen addition by the use of grey and ductile iron casting technology.

Croydon Printing Company Ltd.

# CAST STAINLESS STEEL ALLOY AND METHOD FOR ITS MANUFACTURE

The present invention relates to relatively low-cost stainless steel alloys used for casting applications, e.g. turbine and turbocharger housings, exhaust manifolds, combustion chambers, etc. having satisfactory corrosion resistance and other properties at room and elevated temperatures in the operating range up to 2000°F (1093°C).

Cast articles of this type, in particular, automotive or aircraft turbocharger housings, are subject to elevated operating temperatures up to about

- 10. 2000 °F (1093°C), and must be able to contain a turbine wheel generating very high rotational speeds. In turbochargers for truck diesel engines, the temperature reaches 1300-1400°F (704-760°C) resulting in housing metal temperatures of 1200-1300°F (649-704°G).
- 15. passenger car turbochargers, however, the operating temperatures extend up to the 1750-2000 (954-1909 C) range, which results in metal temperatures of 1550-1950 F (843-1066 C) at the gas inlet or tongue section of the turbocharger housing since this inlet area is
- 20. within a few degrees of the turbine exhaust temperature and is insulated so that heat is not dissipated rapidly. It is in metal sections such as this gas inlet area of an automotive turbocharger where the exhaust gas initially contacts the turbocharger, that
- 25. thermal cracking is encountered, unless relatively expensive stainless steel casting alloys are employed.

The commercially available HD alloy which is inherently a duplex material contains about 26-30% chromium and 4-7% nickel, however, because of the

30.

relatively low nickel content, it is subject to sigma phase formation, which becomes very brittle and gives rise to thermal cracking when used at elevated temperatures, particularly when the cast material is subjected to thermal cycling. In the past, the short

- 5. comings of the HD series alloys have been overcome by adopting a stainless steel casting alloy of higher nickel content such as commercially available high nickel ductile iron casting alloys. Examples of these are NiResist (Trade Mark) developed by International
- 10. Nickel Company, or HK30, a chromium-nickel-iron stainless steel alloy containing approximately 30% chromium and 20% nickel, balance essentially iron. The HK series stainless steel alloys in general have about 18-22% nickel and are fully austenitic. The HK
- stainless steel alloys are some of the strongest stainless steel casting alloys, in terms of creep strength, however, while meeting the high temperature property requirements for turbocharger housings, they are quite expensive and present casting difficulties because of their high nickel content.

US Patent No. 3,969,109 Tanczyn, discloses a stainless steel wrought alloy having a composition of 21-30% Cr, 2-10%Ni, 0.25-0.45%C, 0.01-2.5% Mn and 0.35-0.55% N, in which high temperature strength and

- 25. resistance to sulphidation and oxidation at elevated temperatures are obtained by reducing the carbon and the manganese contents of the commercial 21-4 stainless steel alloys. This patent, however, relates to wrought alloys which are claimed to be fully austenitic. They
- are not therefore cast stainless steel duplex alloys since they are wrought materials and do not enjoy the advantage of a ferrite content.

It is an object of the present invention to provide a low-cost stainless steel casting alloy which is resistant to thermal cracking, and exhibits good room temperature strength and high creep strength and burst resistance at operating temperatures in the range of up to 1950°F (1066°C).

It is also an object of the present invention to provide a relatively low cost stainless steel casting alloy with improved casting characteristics.

It is a further object of the present invention to provide an improved and cost efficient method for casting stainless steel articles for high temperature service.

According to the present invention, there is provided a cast stainless steel article having a duplex 15. metallurgical structure of about 20 - 80% ferrite, the balance being austenite and being substantially devoid of sigma phase, the article comprising essentially in weight percent about 27-31% Chromium, 4-6% Nickel, 0.2-0.5% Nitrogen, 0.2-0.4% Carbon, 0.5-1.5% Columbium, up to 1% Manganese and/or Molybdenum as a sulphide former

0.2-0.4% Sulphur, the balance being Iron, with incidental impurities.

Such an article may have good resistance to thermal cracking when subjected to cycling between room 25. temperature and a service temperature of 1500-1950°F (816-1066°C) and which, in the solution treated condition, may be resistant to oxidation corrosion, may have a room temperature tensile strength of at least 75.000psi and at least about 7% elongation.

30. In accordance with the present invention, therefore a duplex stainless steel alloy, that is, a

two phase alloy having both ferritic and austenitic structure, can be used for cast metal parts subject to high operating temperatures, such as automobile turbocharger housings, gasoline engine exhaust manifolds, and cast furnace or combustion chamber components, thereby combining the high temperature

- 5. components, thereby combining the high temperature properties of the austenitic phase with the castability and low thermal expansion characteristic of the ferritic phase.
- It has been found that the controlled addition of nitrogen to low nickel duplex stainless steels, greatly increases their thermal cracking resistance and effectively improves the stainless steel alloys in a manner normally achieved by higher nickel additions, gaining the strength characteristics, the corrosion
- 15. resistance, and the creep strength of austenitic stainless steels. The resistance of the alloys of the present invention to thermal cracking (due to higher strength and low thermal expansion), by the addition of nitrogen rather than nickel, provides a stainless steel
- 20. casting alloy functionally equivalent to the HK series stainless steels, at substantial cost savings.

Preferably the article has a Nitrogen content of 0.3-0.4 weight percent.

Preferably, the article has a composition

2f. including by weight: 27 - 31% Cr, 4 - 6% Ni, 0.2 - 0.4%C, 0.5 - 1.0% Mn, up to 1.0% Mo, 1 - 2% Si, 0.5 - 1.5% Cb (Columbium), 0.3 - 0.4% N up to 0.03 %P, 0.2 - 0.4 %S, up to 0.50% Cu, up to 0.20% Al, the balance being iron.

Preferably the article has a duplex structure of 40 - 60% ferrite, the balance being austenite.

A preferred composition for the article, by weight may be 31% Chromium, 5% Nickel, 0.24% Carbon, 0.65% Manganese, 1% Silicon, 0.35% Molybdenum, 0.3% Sulphur, 0.9% Columbium, 0.32% Nitrogen, the balance being Iron.

- According to another aspect of the invention,

  there is provided a method for producing a cast
  stainless steel article having a duplex metallurgical
  structure of about 20 80% ferrite, the balance being
  austenite, comprising the steps of: melting a
  commercial steel mixture to a target chemistry of about
- 10. 27 31% Chromium, 4 6% Nickel, 0.2 0.4% Carbon, up to 1% Manganese and/or Molybdenum, 0.5 1.5% Columbium 0.2 0.5% Nitrogen, 0.2 0.4% Sulphur; heating the steel alloy mixture to a temperature of about 2850 2900°F (1566 1593°C) for a time sufficient to
- 15. homogenise the melt; pouring the steel at a tap temperature of about 2850°F (1566°C) into moulds employing gates designed to minimise porosity; and allowing the article to solidify.
- Preferably, the method includes subjecting the

  20. cast article to a solution treatment at about 2000 
  2200°F (1093 1204°C) for 1 4 hours or longer to

  redistribute M<sub>23</sub>C<sub>6</sub> carbide (where "M" is essentially

  Chromium). Preferably, the method includes the step of

  removing the gates by snap breaking after the cast
- 25. article has cooled to room temperature and before the solution treatment. Preferably, the solution treated article is air cooled following the solution treatment and is preferably also subjected to a strengthening treatment at about 1400 1600°F (760 871°C) for up
- 30. to 24 hours.

Thus, a preferred stainless steel casting alloy composition for turbine housings, in accordance with the present invention, is an H-series stainless steel with a relatively low nickel content which is modified with nitrogen to obtain a ferrite/austenite duplex structure having ferrite in the range of 20 - 80%, preferably 40 - 60% ferrite, having improved resistance to thermal cracking. The amount of ferrite present in the alloy microstructure is determined by the chemistry

of the alloy, the fabrication technique, and the heat

10. treatment employed. It is not believed that the ferritic phase contributes to the high temperature properties of the cast alloy.

Without a solution treatment, stainless steel castings according to the invention may be brittle and 15. hence some form of solution treatment is preferable. The brittleness prior to heat treatment has been found to enhance the steel casting method of the present invention, since the cast steel gating can be designed for gate removal by snapping rather than machine 20. cutting. The preferred solution treatment is conducted

at 2000 - 2200°F (1093 - 1204°C) for 1 to 4 hours followed by air cooling. Following the solution treatment, the alloy may be subjected to a strengthening treatment of 1400 - 1600 °F (760 - 871°C) for up to 24 hours, but since the cast articles

encounter temperatures in this temperature range during service, the strengthening treatment may be effected in situ during testing or initial service of the cast articles.

The primary strengthening mechanism of the stainless steel casting of the present invention, is

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believed to be by carbide dispersion in a solid solution strengthened matrix. Of the two types of carbides formed, i.e. MC and M23C6, MC carbide, where "M" is essentially Cb, is relatively unaffected by solution treatment and hence remains as a strengthening

- 5. constituent after solution treatment. The brittle M23C6 carbide constituent, (where "M" is essentially Cr) is spheroidized or partially dissolved during solution treatment. This dissolved carbide reprecipitates at the lower temperatures encountered
- 10. during normal operating conditions and thus enhances the strength of the alloy in service. Thus the solution treatment redistributes, i.e. dissolves or spherioidizes the M<sub>23</sub>C<sub>6</sub> carbide, the spheroidized or droplet from of the carbide being more ductile than the original angular form.

Sulphur is added to the stainless steel casting alloy of the present invention, in an amount of 0.2 - 0.4% to enhance machinability, and is combined with manganese or molybdenum as MnS or MoS. Silicon, which

- 20. adds to the fluidity of the cast alloys, is normally present in commercial steels in an amount up to 2%, and 2.5 1.5% columbium is added for strengthening since columbium produces the very stable MC carbide.

  Tantalum may be similarly beneficial for strengthening
- 25. but is more expensive than columbium.

Another advantage found in the use of the stainless steel alloys of the present invention is involved in the casting procedure. It has been found that the lower cost casting techniques as normally used for casting grey or ductile iron may be employed.

30. for casting grey or ductile iron may be employed.

Steel foundry casting methods are inherently more
expensive than grey iron casting techniques, primarily

because the metal is poured at higher temperatures, of the order of 3100°F (1704°C) in steel foundries, rather than 2600 - 2900°F (1427 - 1593°C) in iron foundries. It was found that the stainless steel of the present invention may be cast at tap temperature (the temperature at which steel is transferred to the pouring ladle) of about 2850°F (1566°C).

The gating practice used in steel foundries involving the use of additional gates, was used in the casting of the alloy of the present invention in order

- 10. to obtain lower porosity and hence better quality castings. Because of the unique chemistry and microstructure of the stainless steel articles cast in accordance with the present invention, snap off gates may be used because of the presence of the brittle
- 15. carbide constituent M<sub>23</sub>C<sub>6</sub>, which partially dissolves during the solution treatment. The presence of this carbide constituent in the as-cast condition permits removal of the gates by snap-break separation, rather than the more expensive gate removal techniques
- 20. involving machining operations, normally used for austenitic type steel castings.

The invention may be carried into practice in various ways and some preferred embodiments will now be illustrated in the following non-limiting examples, and with reference to the following drawings, in which:

Figure 1 is a photomicrograph (at 400%) of a metallographic specimen taken from a stainless steel turbocharger housing, cast in accordance with the present invention having the composition shown for DMS016 with 0.16%n,

Figure 2 is a photomicrograph similar to Figure 1 the composition including 0.20% N;

25.

30.

Figure 3 is a photomicrograph similar to Figure 1 the composition including 0.32% N;

Figure 4 is a photomicrograph similar to Figure 1 the composition including 0.35% N; and

Figure 5 is a simulated model of a turbocharger

5. housing produced on a CAD (computer aided design) unit.

#### EXAMPLES

- Turbine housings were prepared for testing in accordance with the present invention made of the DMS016 alloys shown in Table 1 and the resulting castings had the properties shown in Table II. Table I also shows the compositions of the closely related HC,
- 15. HD and HK series alloys. The pouring temperature varied from 2733 2770°F (1500 1521°C) for twelve (12) ladles poured in connection with the above examples. The charge material was a commercial mixture approximating the desired chemistry of the DMS016 20. alloys in accordance with the invention.

Figure 1 is a 400% photomicrograph, showing the microstructure of alloy DMS016 modified with 0.16%N, at 400% showing approximately 10% austenite, which is the lighter phase, the darker phase being ferrite. The

25. microstructure shown in Figure 2, (0.20%N) contains about 20% austenite, the microstructure shown in Figure 3 (0.32%N) contains about 40 - 50 % Austenite, and the microstructure shown in Figure 4 having 0.35% N contains about 50 - 55% austenite.

TABLE 2

Properties	DMS 016A	DMS 016B	DMS 016 <sup>1</sup>	DMS 016 <sup>2</sup> DMS 016 <sup>2*</sup>
Rm. temp. yield (x1000) psi	78.3 (55.1)	85.3 (60.0)	74.3 (52.2)	74.3 (52.2) 85.2 (59.9) 80.2 (56.4)
"" - Tensile (x1000) psi	(0.89) 7.96	121 (85.1)	119.3 (83.9)	119.3 (83.9) 113.6 (79.9) 107 (75.2)
"" & Elong.	.18	24.4	26	9
17.50°F (954°C) (X1000)psi	15 (10.5)	16.1 (11.3)	13.9 (9.77)	13.9 (9.77) 13.8 (9.70) 13 (9.14)
"" - Tensile (x1000) psi	18.5 (13.0)		14.7 (10.3)	19.9 (14.0) 14.7 (10.3) 15.4 (10.8) 16.4 (11.5)
"" - %Elong.	27	37.8	22	28 .22

\*Properties after exposure to 1500°F (816°C) for 100 hours (substantially same properties exposure at 1750°F (954 °C) after 500 Hours).

Figures in parentheses are the equivalent expressed in Kg/m  $^2$  x  $_{10}^6$ 

TABLE 1

Element	NiResist® Type D5S	HD	HK	DMS 016A	DMS 016B	DMS 0161	0162
υ	1.5-2.3	0.5 max	0.2-0.6	0.1-0.2	0.19	0.16	0.24
Cr	1.6-2.2	26-30	24-28	28-32	29.65	28.39	30.9
Ŋį	34-38	4-7	18-22	4-8	5.47	5.21	5.33
Mn	0.7 max	1.5 max	2.0 max	1.0 max	0.67	0.49	0.65
Si	4.8-5.3	2.0 max		2.0 max	1.72	1.49	06.0
Mo	i	0.5 max	0.5	0.1 max	0.1 max	0.12	0.34
ប	0.06 max	0.01 max	0.01 max 0.04 max	1	ı	0.14	0.28
Сb	i	i	ı	1	1	i .	0.87
z	0.02	0.02	t	i	0.2	0.35	0.32
e Eu	Bal.	Bal	Bal	Bal	Bal.	Bal.	Bal
&Ferrite	1	1	*	ı	20**	40*	45**
&Austenite	i	1	i	ī	20	09	ស

\* Basically austenitic with less than 10% Ferrite.

\*\* Approximated from photomicrograph by line intercept estimation.

\*\*\* 0.035 - 0.098 Mg:

A particular requirement for a turbocharger housing is that it must contain a wheel burst. The containment test is performed to determine whether the turbine housing of the particular alloy will contain a wheel which bursts as the rotating speed is increased in accordance with a particular containment requirement policy. Turbocharger manufacturers typically have several burst containment tests, i.e. for auto (gasoline), diesel and aircraft turbochargers. first two tests are generally similar, while the latter (aircraft) may differ primarily in the use of a 10. mechanically weakened wheel.

> A test of the alloy designated DMS0162, was run on a containment burst test stand. The shaft-wheel was modified to facilitate bursting, in accordance with

- standard aircraft test procedures, by drilling an axial 15. hole in the hub and three holes in the back disc to obtain a three piece hub burst. The turbine inlet temperature was controlled to 1750°F (954°C) at the turbine inlet flange and the turbocharger was
- stabilised for 10 minutes at 97,500 rpm at 1750°F 20. (954°C) turbine inlet temperature. The turbocharger was then rapidly accelerated until the weakened wheel burst at approximately 159,000rpm. The housing was found to contain the wheel burst. The results of this
- test show that a turbocharger housing made of the 25. material of the alloy, identified as DMS016<sup>2</sup>, passes the same burst test as alloy the designated HK 30 plus Cb, which is the current austenitic alloy used for aircraft turbocharger housings.
- A conventional aircraft turbine housing 10, as 30. shown in Figure 5 was cast from the alloy of the

present invention designated DMS016<sup>2</sup> and completed 600 hours of gas stand cyclic durability testing at an inlet temperature of 1750°F (954°C). Visual examination of the unit after completion of 600 hours of testing showed no cracks either at the tongue section 12, shown in Figure 5, or at the top of the volute (gas passage) surface. Hence, the cast housing made of alloy DMS016<sup>2</sup> was found to have excellent

Oxidation testing at 1500°F (816°C) showed a

10. weight loss of 0.03% after 100 hours. The sulphidation test at 1700°F (927°C) showed a weight loss of approximately 0.4% in one hour.

resistance to thermal cracking.

Thermal expansion measurements of the alloy of the present invention showed a linear expansion co-

The turbocharger housing finite element thermal

15. efficient of  $18.6 \times 10^{-6} \text{ C}^{\text{O}}$  (10.1 x  $10^{-6} \text{ F}^{\text{O}}$ ) over the range of  $300 - 1000^{\text{O}}\text{C}$ . This expansion rate is similar to that of HK 30 stainless steel.

stress model shown in Figure 5 compared the standard

NiResist material (D-5S) with a similar housing model constructed of the alloy DMS016<sup>2</sup>, and the results shown in table III, show that while DMS016<sup>2</sup> developed greater stress, it had a greater fatigue life. The temperature at the tongue 12 was 1520°F (827°C) and in the waste

- 25. gate port region 16 was 1480°F (804°C). While these results were based on very limited creep data, the values for which may vary significantly, the data as shown in Table III indicates greater durability in the alloy of the present invention, DMS016<sup>2</sup>.
- The finite element stress analysis identified two distinct critical areas where fatigue cracks are expected to occur, namely the tongue 12 and the waste

gate port region 16. Thus, it was found that DMS016<sup>2</sup> has higher strength at elevated temperatures than D5S (NiResist) and also has a higher modulus of elasticity and a slightly lower co-efficient of thermal expansion. The result is a casting able to withstand higher thermal stress.

#### TABLE III

10.	Config uration	Location	Developed Stress (KSI) (kg/m <sup>2</sup> x 10 <sup>6</sup> )	Fatigue Life minimum	(Cycles) Typical
15.	Base-line	Tongue	22.7 (16.0) 8.8 ( 6.2)	160 880	370 1770
12.	NiResist)	port			. 1770
	Base-line	Tongue	36.5 (27.7)	180	410
20.	using DMS	wastegate	12.0 (8.44)	900	1820
20.	Tempe	ratures -	1520 <sup>o</sup> F (827 <sup>o</sup> C) 1480 <sup>o</sup> F (804 <sup>o</sup> C)		astegate

25.

5.

Five samples of DMS016 with varying amounts of nitrogen, were prepared and subjected to mechanical testing, the results of which are shown in Table IV.

Since a minimum of about 7% of elongation is required for satisfactory ductility, these data indicate about 0.20% minimum nitrogen is required. The elongation

data shown in table IV also show cast samples of DMS016

alloy to be substantially devoid of the brittle sigma phase constituent in DMS016 alloys having a nitrogen content of 0.20% or more. The maximum solubility of N is about 0.6%. At 0.5% N, brittle nitrogen compounds may appear, which will reduce ductility.

## TABLE IV

10.		Yield strength	Ult. tensile	Elongation
	<u>N\$</u>	(0.2% off set)	Strength - Psi	Percent
	0.14	88,500	95,200 (66.9 <u>)</u>	3.0
	0.14	91,900	97,000 (68.2)	2.0
15.	0.16	90,100	96,400 (67.8)	3.0
	0.16	88,600	97,600 (68.6)	3.0
	0.20	90,000	105,800 (74.4)	7.0
	0.20	86,200	103,200 (72.6)	9.0
	0.32	80,200	114,800 (80.7)	11.0
20.	0.32	78,200	113,100 (79.5)	14.0
	0.35	86,200	120,800 (85.0)	13.0
	0.35	81,200	119,600 (84.1)	14.0

Figures in parentheses are the equivalent expressed in 25.  $kg/m^2 \times 10^6$ .

Based upon the experiments performed and the turbine housings exposed to a simulated or actual 30. environment, the DMS016 alloy appears to meet the development guidelines that were established in that it has castability, machinability and service properties

equal to or superior to D5S NiResist and in many areas approaches the properties of HK30 stainless steel, a more expensive high nickel material.

#### CLAIMS:

5.

- 1. A cast stainless steel article having a duplex metallurgical structure of about 20 to 80% ferrite, the balance being austenite, and being substantially devoid of sigma phase the article comprising essentially in weight percent, about 27 31% Chromium, 4 6% Nickel, 0.2 0.5% Nitrogen, 0.2 0.4% Carbon, 0.5 1.5% Columbium, up to 1.0% manganese and/or Molybdenum as a sulphide, 0.2 0.4% Sulphur,
- 10. 2. An article as claimed in Claim 1 characterised by a Nitrogen content of 0.3 - 0.4 weight percent.

the balance being Iron, with incidental impurities.

- An article as claimed in Claim 1 or Claim 2
   characterised by a duplex structure of 40 60% ferrite, the balance being austenite.
- 4. An article as claimed in any preceding claim characterised by consisting essentially by weight of 20. 31% Chromium, 5% Nickel, 0.24% Carbon, 0.65% Manganese, 1% Silicon, 0.35% Molybdenum, 0.3% Sulphur, 0.9% Columbium, 0.32% Nitrogen, the balance being Iron.
- 5. An article as claimed in any preceding claim
  25. characterised by its having been solution treated for 1
  to 4 hours at about 2000 to 2200°F (1093 1204°C).

6. An article as claimed in Claim 5 characterised by its having been air cooled from the solution treatment and subsequently subjected to a strengthening heat treatment at 1400 to 1600°F (760 - 871°C) for up to 24 hours.

5 -

- 7. A method for producing a cast stainless steel article having a duplex metallurgical structure of about 20 80% ferrite, the balance being austenite, comprising the steps of: melting a commercial steel
- 10. mixture to a target chemistry of about 27 31% Chromium, 4 6% Nickel, 0.2 0.4% Carbon, up to 1% Manganese and/or Molybdenum, 0.5 1.5% Columbium, 0.2 0.5% Nitrogen, 0.2 0.4% Sulphur; heating the steel alloy mixture to a temperature of about 2850 2900°F
- 15. (1566 1593°C) for a time sufficient to homogenise the melt; pouring the steel at a tap temperature of about 2850°F (1566°C) into moulds employing gates designed to minimise porosity; and allowing the article to solidify.

20.

- 8. A method as claimed in Claim 7 characterised by subjecting the cast article to a solution treatment at about 2000  $2200^{\circ}$ F (1093  $1204^{\circ}$ C) for 1 4 hours or longer to redistribute  $M_{23}C_6$  carbide (where "M" is essentially Chromium).
- 9. A method as claimed in Claim 8 characterised by the step of removing the gates by snap breaking after the cast article has cooled to room temperature 30. and before the solution treatment.

- 10. A method as claimed in Claim 8 or Claim 9 characterised in that the solution treated article is air cooled following the solution treatment.
- 11. A method as claimed in any of Claims 8 to 10
  5. characterised in that the cast article is subjected to a strengthening treatment at about 1400 1600°F (760 817°C) for up to 24 hours.





FIG. 1

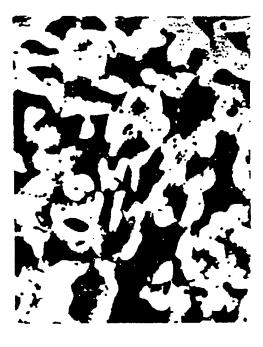


FIG. 2

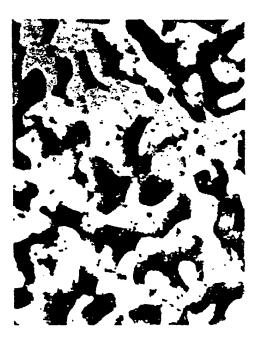


FIG. 3

FIG. 4

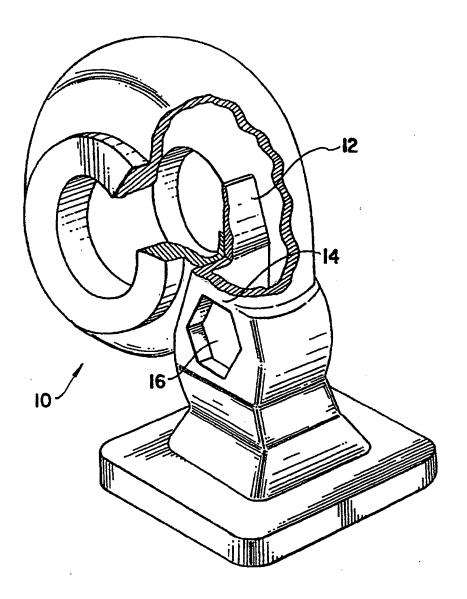


FIG. 5

BNSDOCID. <EP \_\_\_\_\_ 0207697A1 | >



# **EUROPEAN SEARCH REPORT**

0207697

EP 86 30 4758

		SIDERED TO BE RELEVAN	<del></del>	<del></del>
Calegory	of re-	with Indication, where appropriate, levant passages	Relevant to claim	GLASSIFICATION OF THE APPLICATION (Int. CI.4)
A	US-A-3 563 729 * Claims 1,2; 56-63 *	(KOVACH et al.) column 2, lines	1	C 22 C 38/60 C 22 C 38/00 C 22 C 38/48
A,D	19-24 * & FR	 (TANCZYN) 6; column 5, lines -A-2 281 994, & & DE-A-2 535 516	1	·
A	US-A-4 405 389 * Claims 1,2,4,	•	1,5,7,	
				TECHNICAL FIELDS SEARCHED (Int. CI 4)
		•		C 22 C 38
	•			•
1	The present search report has t	een drawn up for all claims		•
T	Place of search HE HAGUE	Date of completion of the search 09-10-1986	LIPPE	Examiner ENS M.H.
r: parti docu l: tech	CATEGORY OF CITED DOCL icularly relevant if taken alone cularly relevant if combined w iment of the same category hological background written disclosure	E: earlier pater after the filli th another D: document c L: document c	nt document, bi ng date ited in the enat	ing the invention of published on, or ication passons